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Viscosity of Picoliter Volumes Measured by Nondegenerate Two-Wave Mixing

by

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Abstract

Using nondegenerate two-wave mixing in colloidal suspensions we measure the viscosity of liquids with as little as 20 picoliters of volume. In addition, changes in the frequency signature with intensity are observed which are interpreted in terms of self-focusing effects.

Typical viscosity measurements require volumes ranging from tens of milliliters to liters of liquid. For many applications in biology, chemistry, and medicine where there may only be very small amounts available, this is impractical. We have developed a technique which measures the absolute viscosity of solutions to within ten percent of previously tabulated values with sample volumes as small as 20 picoliters. This technique relies on the forces associated with radiation pressure. The technique is accurate and not difficult to perform or interpret and is based on the nonlinear optical effect of nondegenerate two-wave mixing (NDTWM).

The systems under consideration are solvents containing suspensions of polystyrene microspheres. In the experiments we performed, the solvents under consideration were mixtures of water and glycerol. A dielectric particle within the solution of interest will feel a force exerted on it in a light field with a strong intensity gradient in the direction of the gradient. The force is given by [1,2,3]:

$$F = \frac{\alpha}{c} \nabla I \qquad (1)$$

where α is the polarizability of the particle, given by

$$\alpha = 4\pi \frac{n^2-1}{n^2+2} a^3 \qquad \text{(MKSA units)} \qquad (2)$$

a being the radius of the particle (900 Å in this work). Nonlinear effects in these artificial Kerr media are caused by the index changes due to density changes in the suspension from the gradient force.[2,3] The nonlinear index predicted from the gradient force is very high and results in effects such as self-focusing, beam trapping, and degenerate four-wave mixing.[2,3] We are interested in the effects caused by a moving index grating from the

interference of two Doppler shifted light beams. The effect was first seen in 1986 by Chang and Sato[4], and studied theoretically by McGraw and Rogovin in 1987.[5]

When two counter-propagating Doppler-shifted light beams are superposed in a nonlinear medium, the travelling intensity grating that results will lead to a travelling index grating. This in turn leads to the scattering of one light beam into the direction of the other; i.e., one beam will gain energy at the expense of the other one. For low intensities, the gain is given by[5]

$$G \sim \frac{\delta\omega\,\tau}{1+(\delta\omega\,\tau)^2} \tag{3}$$

where $\frac{1}{\tau} = 4k^2D$, $k = \frac{2\pi}{\lambda}$, $D = \frac{k_bT}{6\pi\eta a}$ (the diffusion coefficient of the particle in the medium).

At low intensities, the peak gain occurs at $\delta\omega = \frac{1}{\tau}$. Therefore, measurement of two-wave mixing gain as a function of Doppler shift measures the diffusion coefficient of the particle, or equivalently the viscosity of the medium. At higher intensities, the dependence of the gain on frequency is not so simple[5]; the peak depends on a parameter g which is:

$$g = 4\pi \frac{n^2-1}{n^2+2} \frac{a^3}{ck_bT} I \tag{4}$$

This gives the ratio of the strength of the potential the colloidal particle sits in to the average thermal energy in the medium. Figure 1 shows plots of the normalized gain as a function of g and indicates that the peak shifts to higher frequencies as g increases.

Experiments were performed on a suspension of 0.090 μm diameter polystyrene microspheres in glycerol-water solutions. The experimental setup is shown in figure 2. The laser used was a 5 W argon-ion laser running at 514.5 nm. The PZT was driven using

a triangle wave signal at 200 Hz, and the output from the detectors was lock-in detected using as reference an attenuated signal from the function generator driving the PZT. Phase sensitive detection at the PZT displacement frequency insured that we only detected gain antisymmetric in the beam Doppler shift. PZT displacement was calibrated by Michelson interferometry. The diameter of the beam going through the microscope objectives was measured to be approximately 7 μm using pinholes of different sizes. The sample holder was a 275 μm thick 5 microliter volume pipette. The sample volume probed is estimated to be approximately 2×10^{-8} cm^3, or 20 picoliters.

A scope trace of the output from detector 1 is shown in figure 3. The upper trace is proportional to the PZT displacement; the lower is the NDTWM signal. Output from detectors 1 and 2 is shown in figure 4, showing that one beam gains energy at the expense of the other. Figure 5 shows NDTWM signal as a function of beam Doppler shift. The peak of the gain curve shifted to higher frequencies as the laser power was increased. This will be discussed later in detail. Figure 6 is a plot of the dependence of the frequency of the maximum of the gain curve on laser power.

The viscosity of three different solvents was measured by using low laser powers where equation (3) is valid and no intensity effects occur. The solutions were 2/3 by volume microsphere solutions at full bottle concentration ($\rho \sim 10^{14}$ particles/cm^3) and

a.) 1/3 by volume deionized water;

b.) 1/6 by volume water, 1/6 glycerol; and

c.) 1/3 by volume glycerol.

Figure 7 shows two-wave mixing signal as a function of $\delta\omega$ in the three solutions.

The low-power laser peak shown in figure 5 and 7 a should be given by $\delta\omega = 4k^2D$. Peak Doppler shifts were found by doing least-squares fits to the data. The peak is measured to be $\delta\omega = 3115$ sec^{-1} and results in $D = 4.74 \times 10^{-12}$ m^2/sec, leading to a prediction of the viscosity $\eta = 0.93 \times 10^{-3}$ kg/m-sec. From the CRC Handbook of Chemistry and Physics[6] the viscosity of water at 24 °C (ambient temperature) is

0.911×10^{-3} kg/m-sec. The following table shows the the measured values vs. the tabulated values from the Handbook of Chemistry and Physics[6]. The agreement is within 10% at all three measured points.

% Glycerol	η_{meas}	η_{HCP}	η in units of 10^{-3} kg/m-sec
0	0.93	0.911	
16	1.39	1.52	
33	2.50	2.62	

Having established that at low powers the position of the peak gain is well understood, there remains the fact that the peak shifts at higher powers. McGraw and Rogovin's theory predicts that the peak position should shift for g>1. We can estimate g from the measured laser power and spot size of the focused beam, giving

$$g \approx 4 \frac{n^2-1}{n^2+2} \frac{a^3}{ck_bT} \frac{P}{d^2} \approx 1.2\,P \quad (P \text{ in watts}) \tag{5}$$

where d is the beam radius (~10 μm). This predicts a maximum value of g of 0.12. Therefore, the theory presented in reference 5 cannot explain the shift in peak. In reference 4 the shift in peak position was called a "change in the diffusion coefficient with laser power", but no mechanism was invoked to explain this.

We believe that self-focusing is responsible for the shift in the frequency of peak gain. If self-focusing occurs, beam intensity will increase leading to greatly enhanced values of g. The self-focusing threshold power for a nonlinear medium is intensity-independent, and is given by the approximate expression[7]:

$$P_{cr} \approx \frac{n_0 \lambda^2}{\pi n_2} \tag{6}$$

The nonlinear index is given by the following expression:

$$n_2 = \frac{4\pi}{ck_bT}\frac{n^2-1}{n^2+2}a^3\rho_0 V_{ball}(n_b - n_w) \qquad (7)$$

where $n = \frac{n_b}{n_w}$, ρ_0 the average particle density, and V_{ball} is the volume of a colloidal particle. From the expression above, $n_2 = 4x10^{-11}$ m^2/W, leading to $P_{cr} \sim 20$ mW. This is around the power where the peak in the gain curve begins to shift to higher frequencies.

To test this we solved the wave equation using a computer program developed at our lab[8]. The program solves the nonlinear wave equation using the semi-spectral method. Using realistic values for the nonlinear index and an assumed Gaussian input beam profile, increases in intensity of 15-30 times were predicted by the code (which was run on an IBM 3280 computer). This increase is just what is needed to raise g to the values that lead to an intensity dependent peak frequency. Figure 8 plots the peak as a function of g from Rogovin's theory and the peak values seen vs. g from the computer model. The results are seen to be fairly accurate.

We have demonstrated that two-wave mixing can be used to accurately measure the viscosity of solutions of water and glycerol. The polystyrene microspheres can be easily transferred from aqueous solution to other liquids via dialysis, allowing viscosity measurements to be made in a variety of solvents. The extremely small volume required renders the technique attractive for work where only small volumes of liquid are available. In addition, we have shown that the self-focusing threshold is measurable by the power at which the peak of the NDTWM gain curve shifts. As analytic expressions for the self-focusing threshold are only approximate, this gives another method for accurate experimental determination of threshold power.

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3. Smith, P.W., Maloney, P.J., and Ashkin, A., Optics Letters, 7 (1982) 347

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Figure Captions

Figure 1 NDTWM gain as a function of g. Gain is normalized by $\frac{1}{\rho g}$. (After ref. 5)

Figure 2 Experimental setup. B is a 50/50 beamsplitter, PZT is a mirror mounted on a piezoelectric transducer, M are 10x microscope objectives, and P is the sample holder, a 5 microliter volume pipette.

Figure 3 Scope trace of NDTWM gain. The upper trace is the ramp voltage for the PZT; the lower is signal from detector 1. As gain is dependent on beam doppler shift, the lower trace should look like the derivative of the upper. The time scale is 1 ms/div.

Figure 4 Top trace: detector 1 signal. Bottom trace: detector 2. Time scale is 2 ms/div.

Figure 5 NDTWM gain as a function of beam doppler shift

Figure 6 Dependence of the peak of the gain curve on laser power

Figure 7 Two wave mixing gain in three solutions.

The solutions were 2/3 0.090 μm microspheres in deionized water with

a) 1/3 water

b) 1/6 water, 1/6 glycerol

c)1/3 glycerol

Figure 8 Normalized frequency of peak gain vs. g

a) From McGraw and Rogovin's theory (ref. 5)

b) Calculated from self-focusing model and experiment (cf. fig. 6)

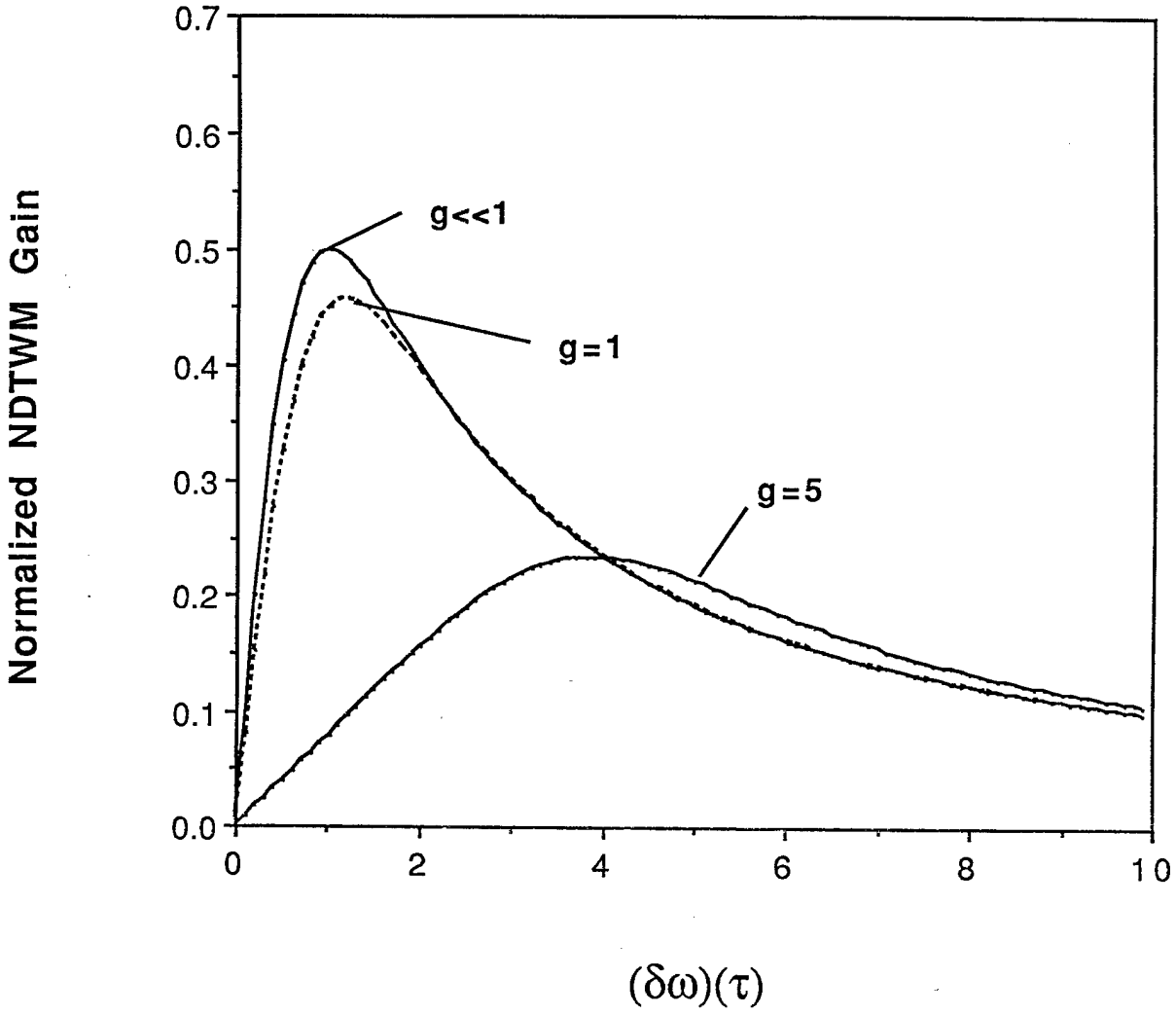

Normalized NDTWM Gain
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
g<<1
g=1
g=5
(δω)(τ)

FIGURE 1

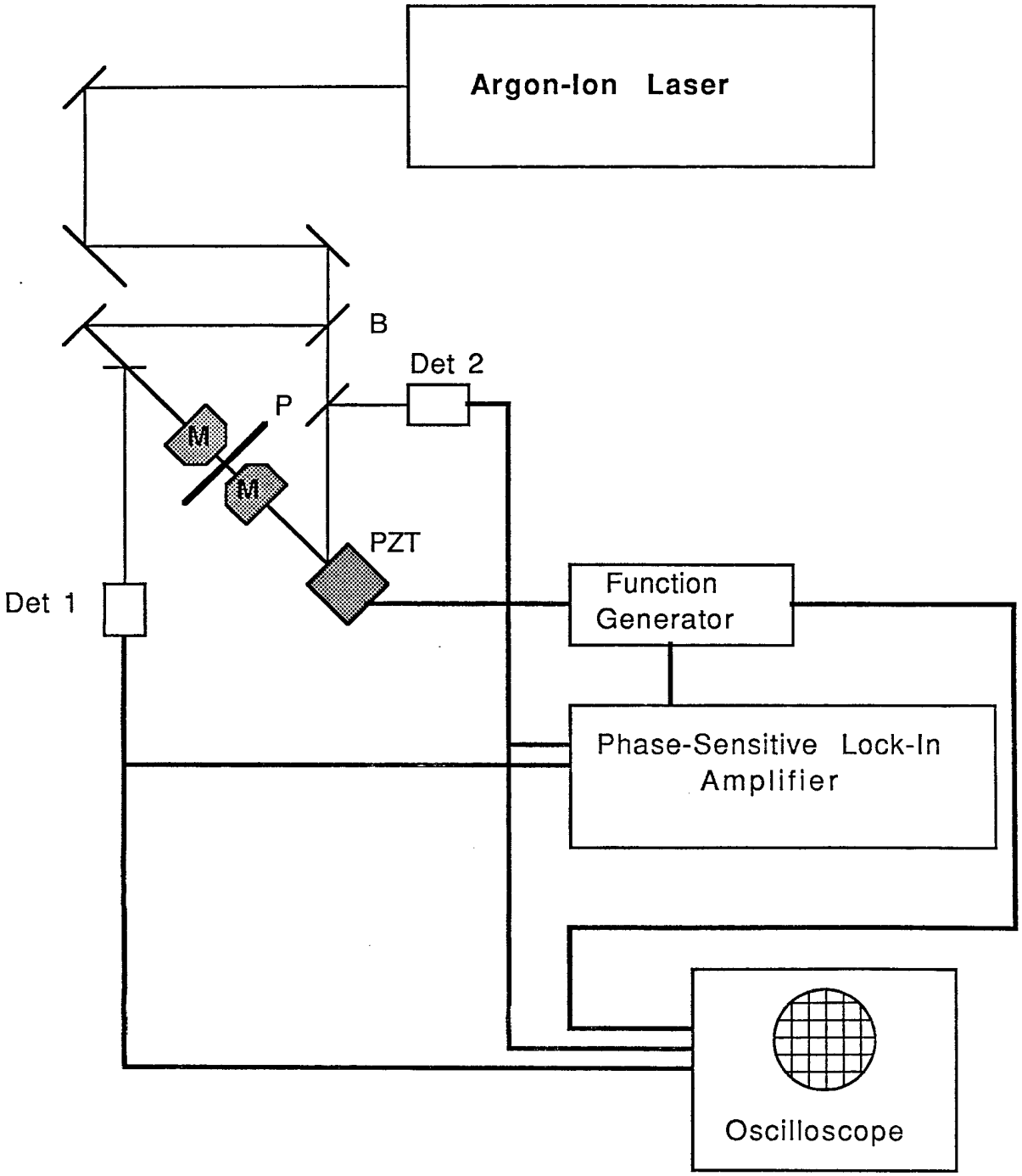

Argon-Ion Laser
B
Det 2
P
M
M
PZT
Det 1
Function Generator
Phase-Sensitive Lock-In Amplifier
Oscilloscope

FIGURE 2

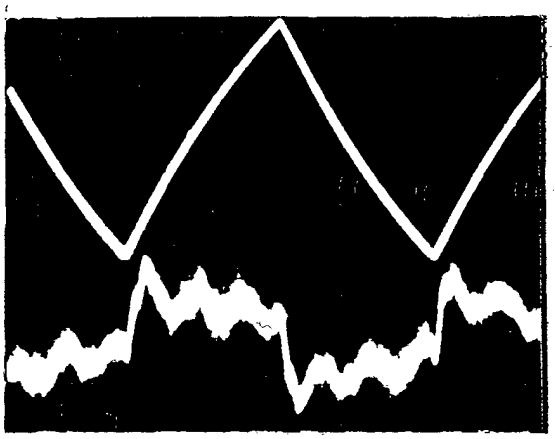


FIGURE 3

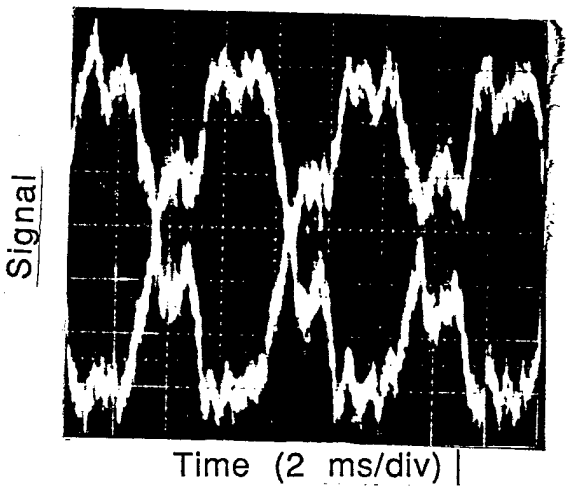


FIGURE 4

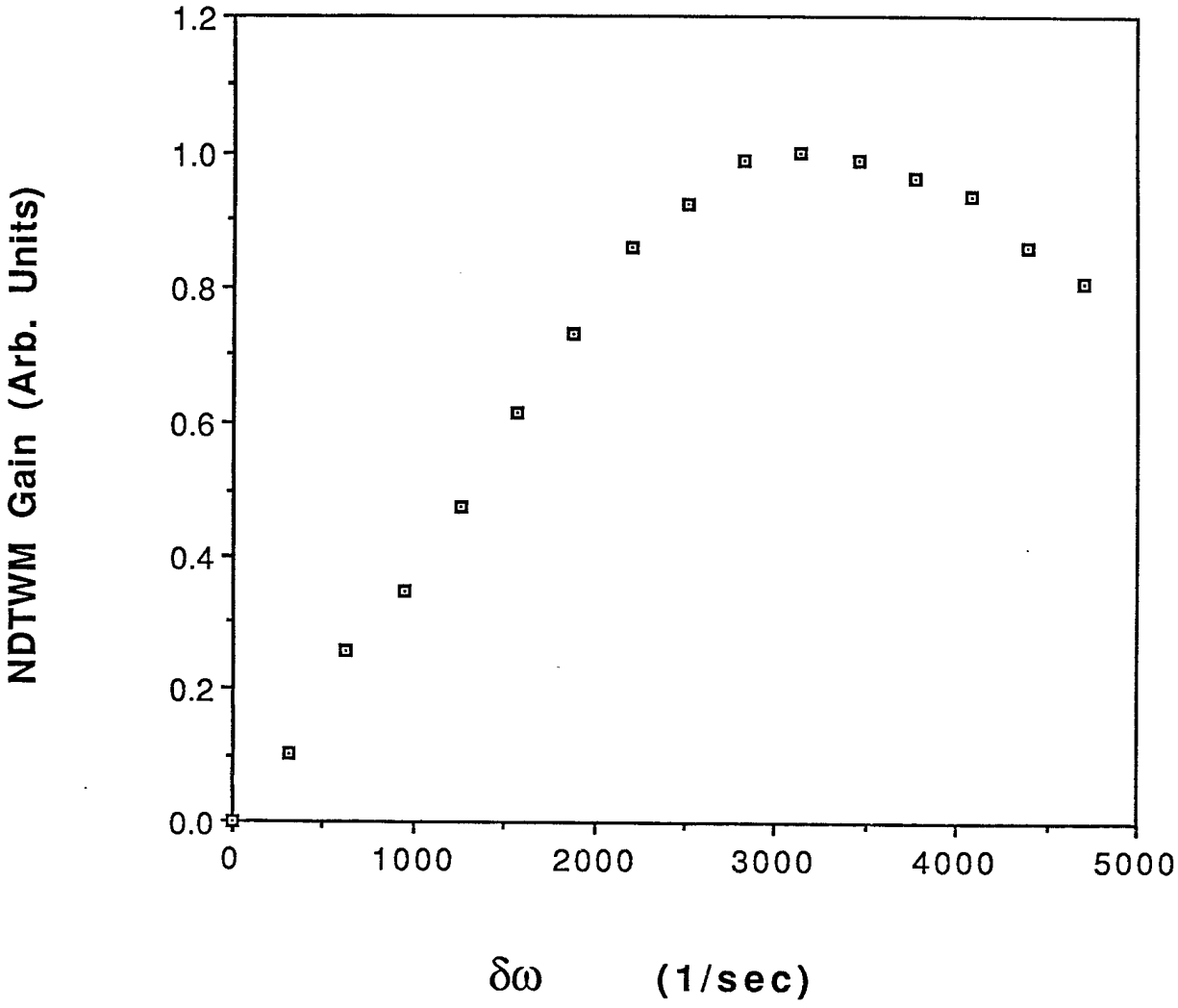

NDTWM Gain (Arb. Units)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1000
2000
3000
4000
5000
δω (1/sec)

FIGURE 5

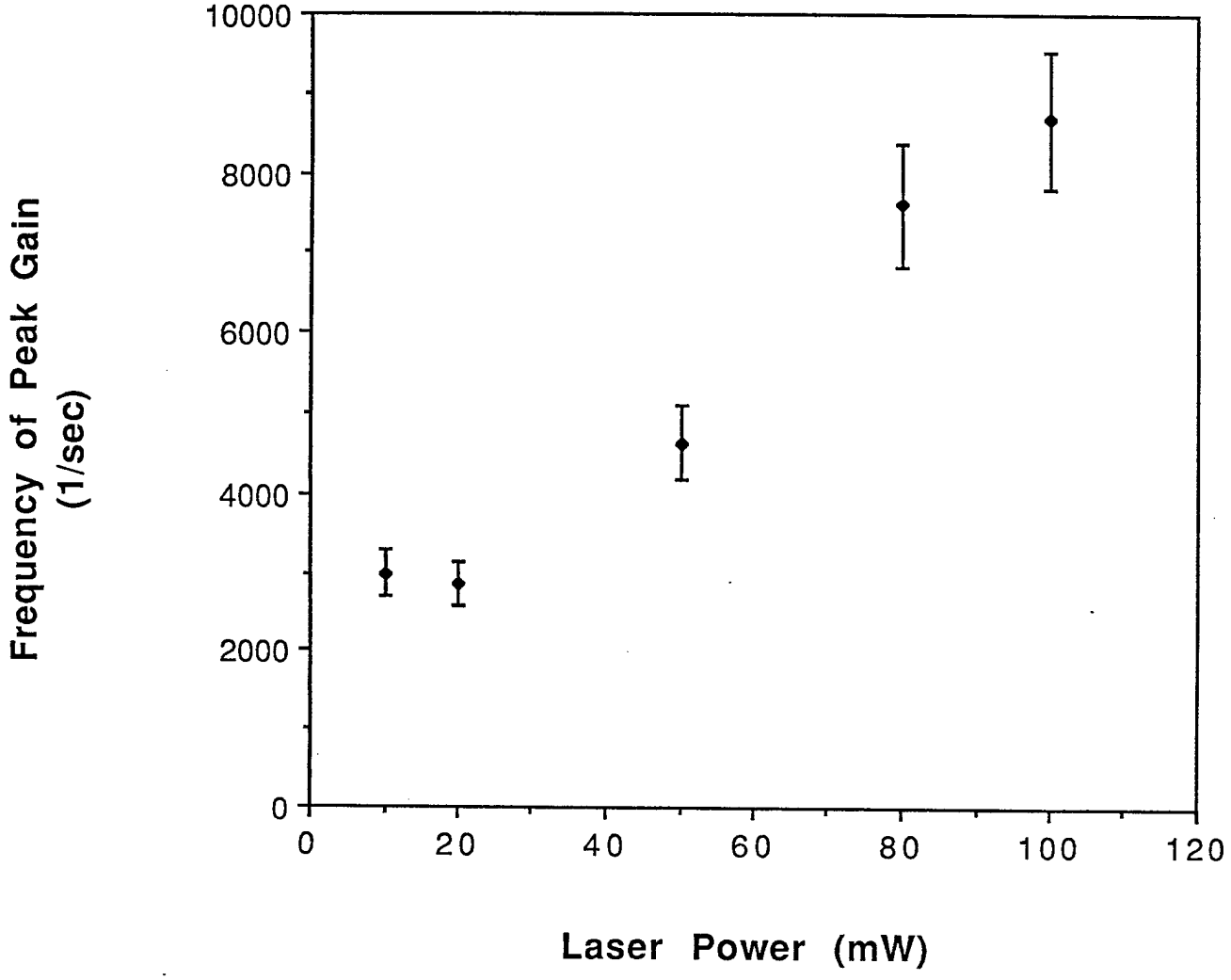
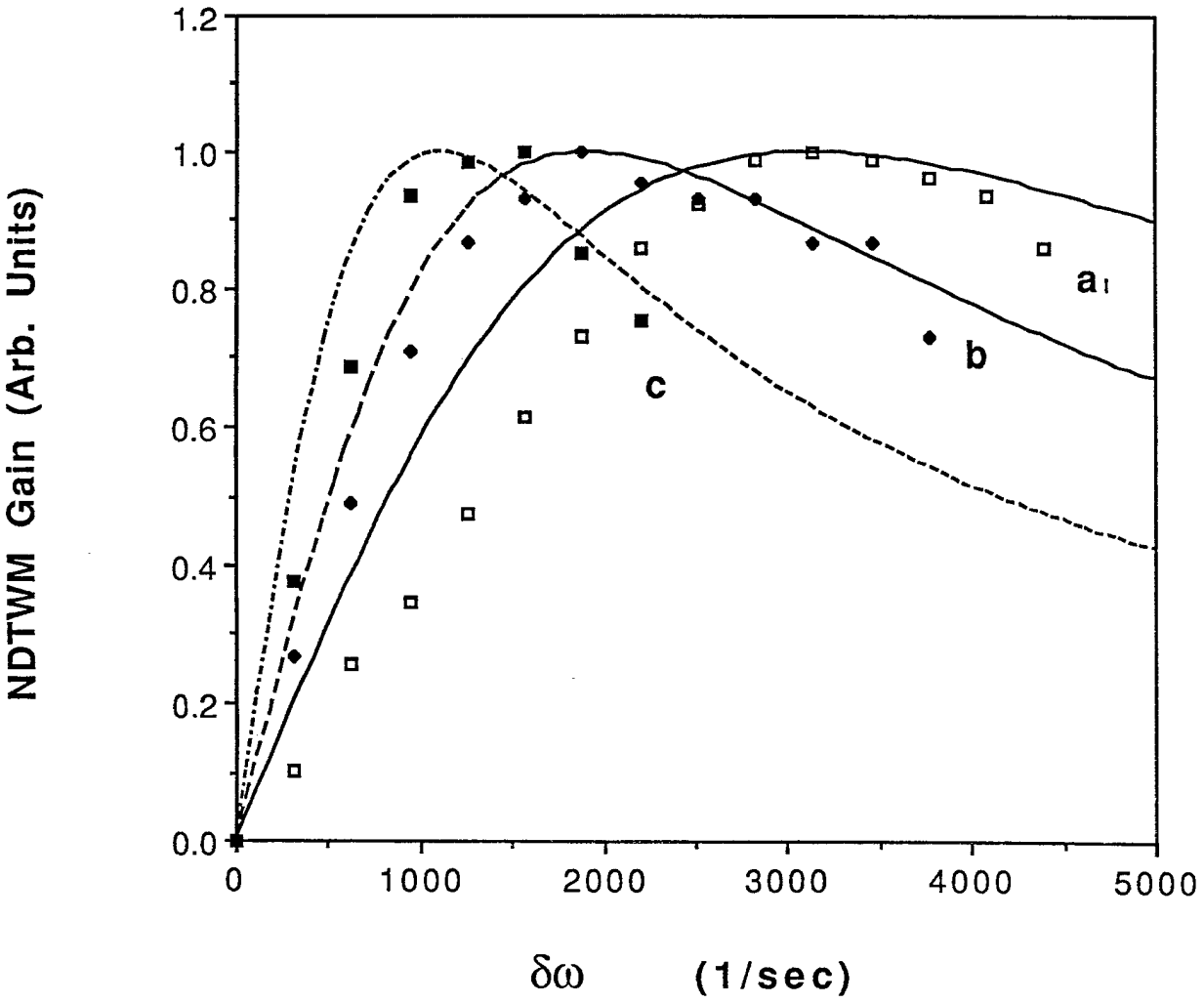

Frequency of Peak Gain
(1/sec)
10000
8000
6000
4000
2000
0
0
20
40
60
80
100
120
Laser Power (mW)

FIGURE #6


NDTWM Gain (Arb. Units)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1000
2000
3000
4000
5000
δω (1/sec)
a
b
c

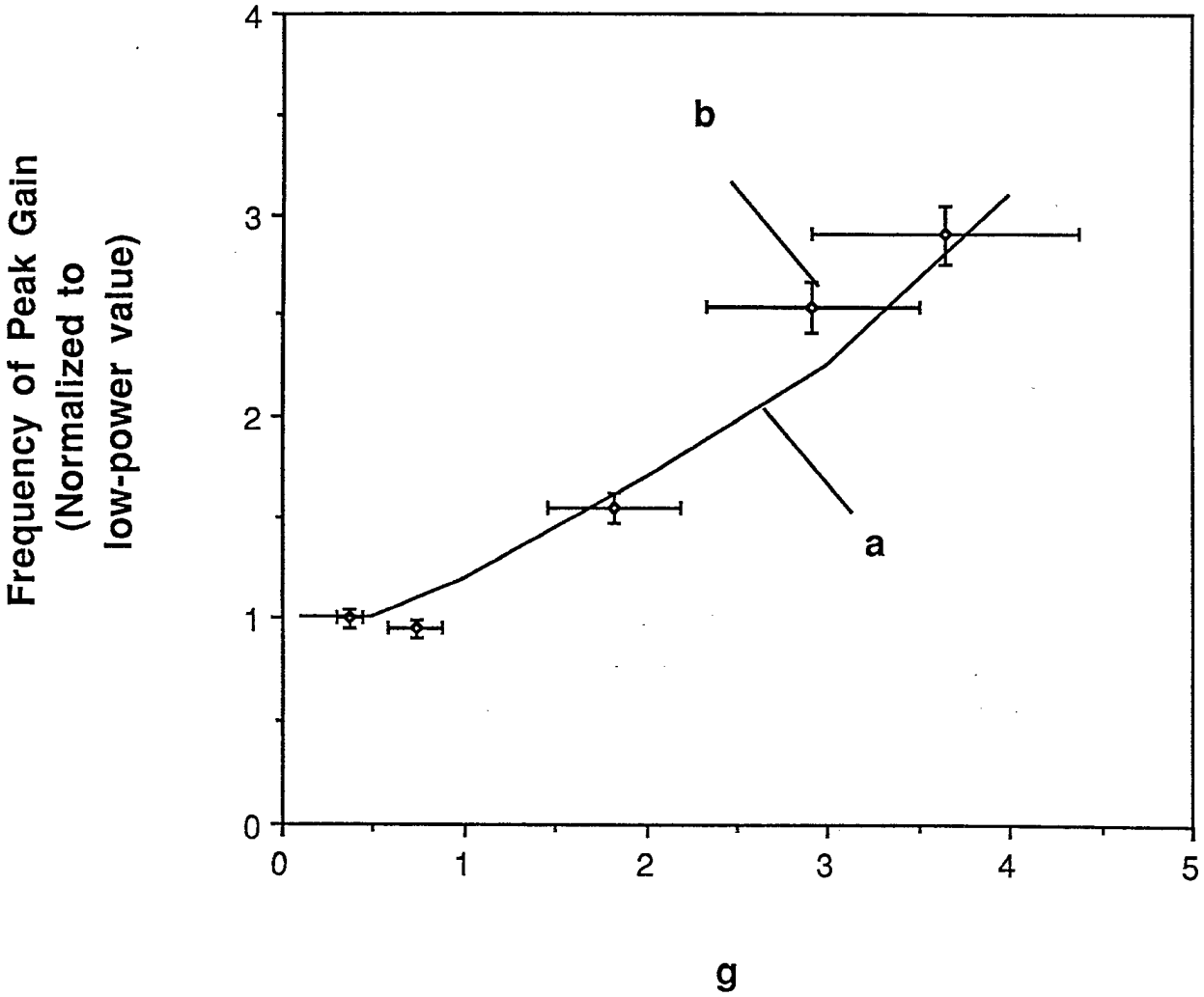

Frequency of Peak Gain
(Normalized to
low-power value)
4
3
2
1
0
0
1
2
3
4
5
b
a
g

FIGURE 5